Semicond. Sci. Technol. 8 (1993) S1–S5. Printed in the UK

OPENING ADDRESS

Prospects for the future of narrow bandgap materials

T C McGill and D A Collins

T J Watson Sr Laboratory of Applied Physics, California Institute of Technology, Pasadena, California 91125, USA

Abstract. Recently there has been greatly expanded interest in narrow bandgap materials. Modern epitaxial techniques and the growing interest in nanostructures have provided areas of application for some of the unique properties of the narrow bandgap material. As always, one of the primary sources of interest is the small bandgap, which makes them the material of choice for many applications in the infrared. However, in recent years their other unique properties have been the basis for a broader set of interests in narrow bandgap semiconductors. The type II band offsets (InAs/GaSb) have been the basis for novel tunnel devices and infrared superlattices. The very small effective masses inherent in small bandgap materials make them the obvious candidates in which to observe quantum confinement effects at larger dimensions than in materials of larger effective mass and wider gap. The ease of making electrical contact to some of the materials (ohmic contact to n-InAs) has made them the material of choice for electrical nanostructures. The ability to put in large amounts of magnetic ions to make magnetic semiconductors has led to a number of novel properties. The technical importance of a narrow bandgap and the unique applications promised by some of the other properties of these materials bode well for substantial research in narrow bandgap semiconductors well into the next decade.

1. Introduction

Beginning with the pioneering work of R A Smith at RSRE, who employed PbS for infrared detection in the 1940s [1], narrow bandgap materials have been the basis for sources and detectors in the infrared. The uses of InAs [2], InSb [3], PbSnTe [4] and HgCdTe [5] for these applications are all well known to this community. However, in recent years these narrow bandgap materials have become interesting because of some of their other properties. The possibility of small masses, high conductivities, unique band offsets and surface properties have made these materials of great interest to the quantum device physicist. These new applications plus some very novel applications of modern superlattice techniques for the infrared have created further interest in narrow bandgap systems.

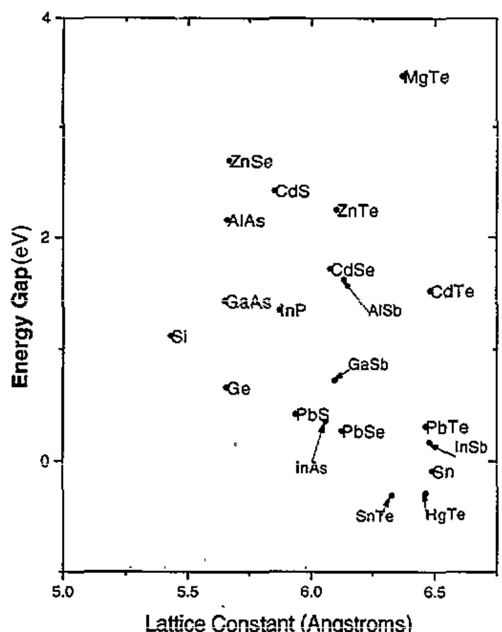

Figure 1. The energy bandgap against lattice constant for some of the relevant 'narrow' bandgap semiconductors. The groupings about a given value of the lattice constant lead to a set of nearly lattice-matched heterojunctions.

2. Important properties

Most discussions of modern semiconductor physics begin with the plot of bandgap against lattice constant (see figure 1). Examination of such data shows the characteristic grouping of materials with similar lattice constants, leading to some of the very exciting near-lattice-matched heterojunctions in systems like HgTe/CdTe [6], InSb/Sn [7] and InAs/GaSb/AlSb [8] (see discussion below) to name just a few. These heterojunction systems are the basis for much of the superlattice and quantum well research currently being carried out on narrow bandgap systems.

In addition, the narrow bandgap semiconductors have a number of other very important properties. These include small effective masses for light holes and conduction electrons, unusual surface and interface properties, and the possibility of incorporating tens of percent of magnetic ions such as Fe and Mn.

Simple $\boldsymbol{k}\cdot\boldsymbol{p}$ theory says that a small effective mass is naturally connected with a small gap [9]. The effective mass for the conduction band and light hole semiconductors in the case of zinc blende systems is given by

$$\text{Effective mass} \sim \text{Energy gap}.$$

Hence, small gap naturally means small mass. For example, for the sequence GaAs, InAs, InSb with bandgaps at room temperature of roughly 1.43, 0.36 and 0.18 eV respectively, the conduction band effective masses are 0.065, 0.025 and 0.014 [10].

Yet perhaps the most unusual features of the narrow bandgap semiconductors are found in their surface and interface properties. For wider bandgap materials, many of the relevant energy positions for interfaces are in the gap. For example, the position of the metal Fermi energy at metal–semiconductor interfaces is typically located well inside the gap of the semiconductor, leading to the typical Schottky barrier behaviour. With small bandgaps, the possible locations of these energies within the gap are more restricted because of the narrow gap, leading to some rather unusual positions for the interface energies. The position for Fermi level pinning for InAs and the band offsets for heterojunctions involving InAs/GaSb/AlSb are illustrated in figure 2. For InAs the pinning position for the Fermi level is in the conduction band leading to a negative Schottky barrier of 122 meV [11] and a great tendency for the InAs surface to invert. For the near-lattice-matched heterojunction system of InAs/GaSb/AlSb, the band offset [12] (shown in figure 2) is such that the conduction band of the InAs is below the valence band of the GaSb, leading to the cross gap or type II heterojunction behaviour. The band offset of AlSb with respect to InAs and GaSb is such that it produces a barrier between the conduction band of InAs and the valence band of GaSb. Further, it would act as a barrier between two layers of GaSb or two layers of InAs.

The diluted magnetic semiconductors offer a special case of systems with unique properties [13]. Many of the narrow bandgap II–VI and IV–VI semiconductors alloy with magnetic ions, notably Mn and Fe, to a few tens of percent. The interaction of these magnetic ions (randomly arranged on the cation sites) with the electrons and holes in the narrow bandgap semiconductor leads to systems with very large magnetic response.

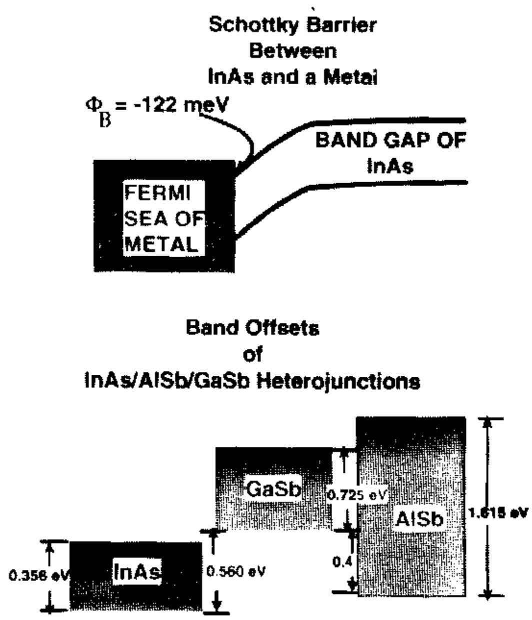

Figure 2. The unusual interface properties of some of the narrow bandgap semiconductors. The Schottky barrier between InAs and metals is negative. The heterojunction band offsets for the InAs/GaSb heterojunctions are such that the bottom of the conduction band of InAs sits below the top of the valence band of GaSb.

3. Applications

The number of applications of these narrow bandgap materials has been increasing rapidly over the last couple of years. Applications are found not only in the detection and generation of infrared radiation but more recently as the active regions of quantum devices.

3.1. Narrow bandgap for infrared optoelectronics

The biggest single application of the narrow bandgap systems has been as infrared sources and detectors. The use of these materials as detectors for the military is well known and amply illustrated by recent television coverage. However, the military uses of the infrared are not the only applications for sources and detectors in this wavelength range. Monitoring the properties of the earth both with respect to temperature (global warming) and chemically requires very advanced detectors that are suitably reliable for application in satellites for surveillance of the earth from space [14]. This application as detectors is the driving force of research in narrow bandgap systems. Observation of the heavens in the infrared is giving us a whole new view of the constituents of our universe [15]. The most appropriate wavelength range for searching for nearby planetary systems is the infrared since in this spectral range the brightness of a planet is more nearly equal to that of the star which the planet is circling [16]. Spectrally resolved active and passive infrared systems show promise as the chemically sensitive environmental monitoring system of the future [17]. The push to produce highly controlled industrial processes may find a partial solution to the monitoring of temperature, chemical composition and other key process-sensitive parameters by the application of infrared imagers [18]. The future requirements for energy efficiency will make infrared imaging a routine technique for discovering potential energy leaks in housing and other structures and processes. All of these future applications bode well for the unique niche that the infrared materials fill. The venerable Pb salts continue to play a role as sources and detector arrays. The performance of HgCdTe alloys throughout the 3–12 μm infrared bands makes them the likely choice for infrared imagers in the short term. The III–V quantum well approach promises to provide the benefits of a III–V technology to make possible large pixel arrays of infrared imagers but with performance substantially less than in those using intrinsic gap materials. The recently proposed InAs/GaInSb [19] superlattice promises to provide infrared imagers [20] with performance comparable to or better than that of HgCdTe [21] in a III–V based materials technology.

3.2. Quantum devices

It is fairly widely recognized that we will see a paradigm shift in the way that we produce electronic computers. The old strategy of simply shrinking the transistors will begin to fail in the early part of the next century [22]. For continued improvement in the performance curve for modern electronics a new strategy will have to be developed. That new strategy is likely to involve the application of heterojunction devices that are capable of being shrunk to even smaller dimensions. There are a number of advantages that narrow band materials have for application in the quantum devices. Some of these are: small effective mass; high conductivity; ease of obtaining large subband splitting; and ease of making ohmic contacts. To illustrate the role of small effective masses, we have plotted the temperature at which the subband splitting between the two lowest levels is equal to $k_B T$ in figure 3. This is simply a calculation of

$$\frac{\hbar^2 \pi^2}{2m^* k_B d^2}.$$

To demonstrate the wide variety of two-terminal tunnel devices, we have illustrated ten different negative resistance devices in figure 4. All of these devices have been demonstrated experimentally over the last couple of years [23]. The device shown in figure 4(A) currently holds all of the performance records for two-terminal tunnel devices. Frequencies as high as 1.2 THz have been projected [24]. The devices in figures 4(B) and 4(C) are examples of the so-called 'resonant interband tunnelling device'. In the electron version of this device (figure 4(B)), electrons tunnel from the InAs conduction band through an AlSb barrier into resonances in the GaSb valence band, then through the second AlSb barrier into the second layer of InAs. This device has a very large

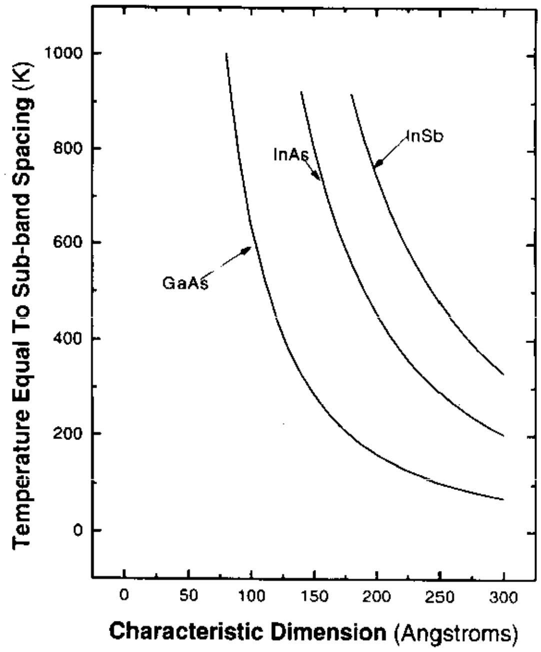

Figure 3. The subband spacing for infinite quantum wells made up of GaAs, InAs and InSb. The materials with the smaller bandgaps (InSb and InAs) and consequently the smaller effective masses are seen to have splittings that are equivalent to $k_B T$ at characteristic dimensions that are much larger than for GaAs with a larger bandgap and greater mass.

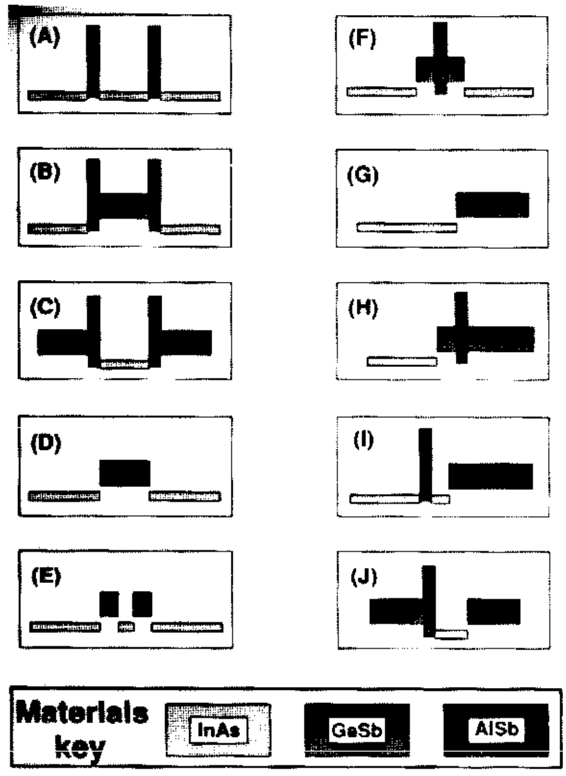

Figure 4. Schematic illustration of the heterojunction layers for ten different two-terminal tunnel devices that have been fabricated in the InAs/GaSb/AlSb near-lattice-matched heterojunction system.

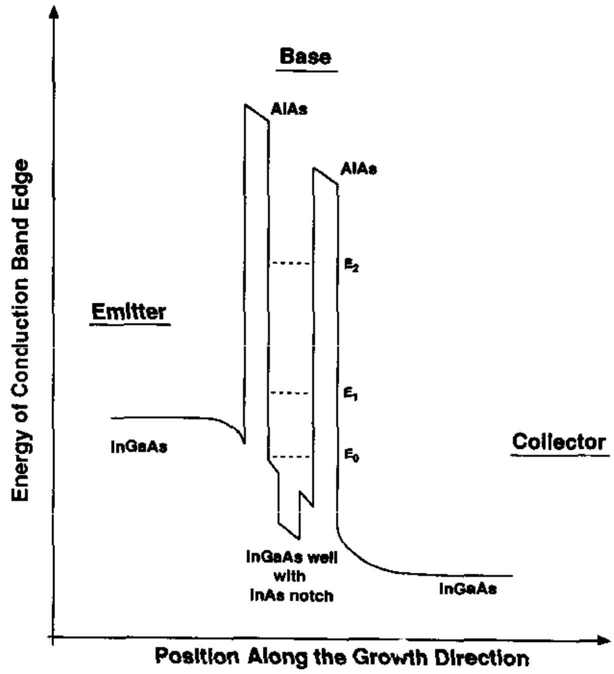

Figure 5. The schematic diagram of a three-terminal tunnel device. The electrons tunnel from an InGaAs emitter through a base with an InAs notch into an InGaAs collector. The base layer is very narrow. The InAs notch both improves the conductivity and makes it easy to establish an ohmic contact to the very narrow layer.

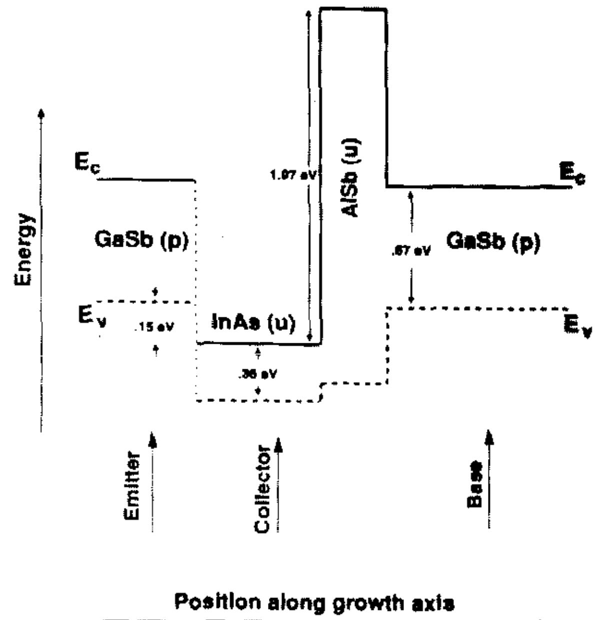

Figure 6. The so-called 'Stark effect' transistor. The device functions by the modulation of the position of the subbands in the InAs collector layer due to a 'Stark' effect shift induced by the applied base potential.

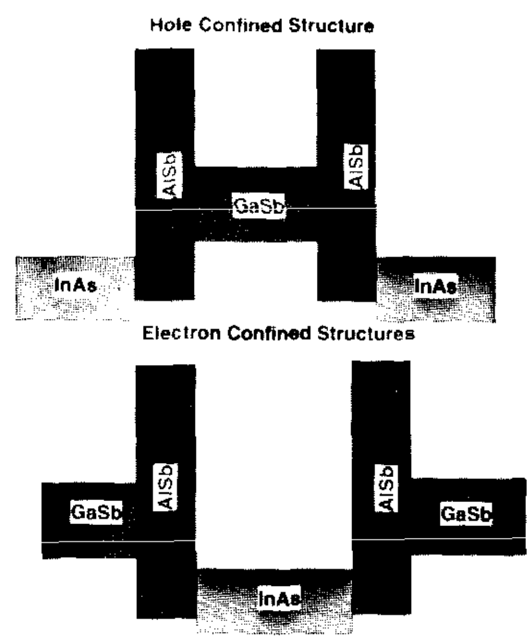

Figure 7. Schematic diagram of 'leaky' quantum wires and dots. The unique band offsets in the InAs/GaSb/AlSb heterojunction system puts the energies of electrons and holes at roughly the same level, making possible a whole set of complementary quantum device structures.

peak-to-valley ratio for the negative resistance region of the current–voltage characteristic. This particular attribute has made it the most desirable device for application as elements in quantum device-based logic and fuse-based artificial retinas. In addition to the two-terminal devices shown here, the narrow bandgap systems have played a major role in the fabrication of three-terminal quantum devices. Investigators at Texas Instruments [25], have successfully fabricated devices originally proposed by Schulman and Waldner [26]. A typical device is shown in figure 5. The fact that it is so easy to make an ohmic contact to InAs has been exploited by this group to produce an acceptable ohmic contact to a 50 Å thick layer that forms the base of this device. Other three-terminal quantum devices have been fabricated by using narrow bandgap systems. The most successful demonstration of the Stark effect transistor employed the InAs/AlSb/GaSb heterojunction system. In figure 6 we show a schematic diagram of the structure of the Stark effect transistor [27] This structure takes advantage of the highly transparent GaSb/InAs interface and the ease of making contact to the InAs layer. The device shows the largest current gain observed at room temperature for a three-terminal quantum device.

This same InAs/AlSb/GaSb heterojunction system promises to be a nearly ideal system for quantum dots and quantum wires. The small effective mass of the InAs and GaSb means that quantum size effects will occur at a much larger thickness, making the nanofabrication process simpler. The occurrence of holes in the GaSb and electrons in the InAs at roughly the same energies suggests that we could make devices with leaky quantum wires and dots as illustrated in figure 7.

3.3. Narrow bandgap diluted magnetic semiconductors

The subject of diluted magnetic semiconductors has recently been the subject of a very extensive review [13]. We strongly recommend that those interested in the details of this subject consult this review. However, suffice it to say that the unique combination of magnetic response and narrow gap has given these materials unique properties, including a bandgap that is tunable in a magnetic field and very large magnetoresistance.

4. Summary

The future is very bright for narrow bandgap systems. The historical role they have played as infrared sources and detectors is likely to be enhanced as the infrared spectal region finds progressively greater application in earth observation systems, infrared astronomy, environmental monitoring systems, process control systems and commercial applications. The small effective mass and unique surface and interface properties make narrow bandgap heterojunction systems the candidates of choice for quantum devices. The unique magnetic response of the small effective mass systems, along with the solubility of magnetic ions in some of the narrow bandgap materials, makes them the obvious candidates for many applications in which magnetic fields could play a role.

Acknowledgments

The authors gratefully acknowledge discussions of all aspects of this work with D H Chow (Hughes Research Labs), J R Söderström (Ericsson), D L Smith (Los Alamos National Lab), R H Miles (Hughes Research Labs), H Ehrenreich (Harvard), R W Grant (Rockwell/ Caltech), T Fu, J O McCaldin, D Z Ting, R Marquardt and Y X Liu (all Caltech). Financial support provided by the Office of Naval Research, Air Force Office of Scientific Research and Defense Advanced Research Projects Agency is gratefully acknowledged.

References

[1] Smith R A, Chasmar R P and Jones F E 1957 *The Description and Measurement of Infrared Radiation* (New York: Oxford University Press)
[2] See, for example, Limperis T and Mudar J 1989 *The Infrared Handbook* revised edn, ed W L Wolfe and G J Zissis (Ann Arbor, MI: Infrared Information Analysis Center) p 11-76–11-77
[3] See, for example, Kruse P W 1970 *Semiconductors and Semimetals* vol 5 ed R K Willardson and A C Beer (New York: Academic) pp 15–70
[4] For a recent review see Zoog H, Malssen C, Masek J, Hoshino T, Blunier S and Tiwari A N 1991 *Semicond. Sci. Technol.* **6** C36
[5] See, for example, Dornhaus R and Nimtz G 1983 *Narrow-Gap Semiconductors* (Berlin: Springer) pp 119–304
[6] Sculman J N and McGill T C 1979 *Appl. Phys. Lett.* **34** 663
Smith D L, Schulman J N and McGill T C 1983 *Appl. Phys. Lett.* **43** 180
[7] See, for example, Stradling R A 1991 *Proc. SPIE* **1361** 630
[8] See, for example, Ohno H, Esaki L and Mendez E E 1992 *Appl. Phys. Lett.* **60** 3153
[9] Kittel C 1963 *Quantum Theory of Solids* (New York: Wiley) p 186
Kane E O 1957 *J. Phys. Chem. Solids* **1** 249
[10] See, for example, *Some Important Properties of Semiconductor Materials* 1971 (St Peters, MO: Monsanto Electronic Materials)
[11] Mead C A and Spitzer W G 1964 *Phys. Rev.* **134** A713
Weider H 1981 *Appl. Phys. Lett.* **38** 170
[12] For a general review on band offsets and the literature see Yu E T, McCaldin J O and McGill T C 1992 *Solid State Physics* ed C Seitz *et al* (New York: Academic) vol 46
[13] Furdayna J and Kossut J 1991 *Semiconductors and Semimetals* vol 25 ed R K Willardson and A C Beer (New York: Academic)
[14] Schmugge T J, Becker F and Li Z L 1991 *Remote Sens. Environ.* **35** 95
[15] Neugebauer G and Becklin E E 1973 *Sci. Am.* **228** (4) 28
[16] Cutts J A and Capps R W 1990 *Proc. 4th Int. Conf. on Advanced Infrared Detectors and Systems* (Conf. Publ. No 321) (London: IEE)
[17] See, for example, Ness S A 1991 *Air Monitoring for Toxic Exposures: An Integrated Approach* (New York: Van Nostrand Reinhold)
[18] Norton P, private communication
[19] Mailhiot C and Smith D L 1987 *J. Appl. Phys.* **62** 2546
[20] Miles R H, Chow D H, Schulman J N and McGill T C 1990 *Appl. Phys. Lett.* **57** 801
Miles R H, Chow D H and McGill T C 1993 *Semicond. Sci. Technol.* **8** S102
[21] Grein C H, Young P M and Ehrenreich H 1992 *Appl. Phys. Lett.* submitted for publication
[22] See, for example, Bate R T 1988 *Sci. Am.* **258** (3) 78
[23] Collins D A, Chow D H, Yu E T, Ting D Z-Y, Söderström J R, Rajakarunanayake Y and McGill T C 1991 *Resonant Tunneling in Semiconductors: Physics and Applications* ed L L Chang *et al* (New York: Plenum) pp 515–28
[24] Brown, E R, Söderström J R, Parker C D, Mahoney L J, Molvar K M and McGill T C 1991 *Appl. Phys. Lett.* **58** 2291
[25] Seabaugh A, Kao Y-C, Randall J, Frensley W and Khatibzadeh A 1990 *Extended Abstracts of the 22nd (1990 Int.) Conf. on Solid State Devices and Materials, Sendai* (Japan Soc. Appl. Phys.) pp 15–18
[26] Schulman J N and Waldner M 1988 *J. Appl. Phys.* **63** 2859
[27] Collins D A, Chow D H and McGill T C 1991 *Appl. Phys. Lett.* **58** 1673